



(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) Publication number:

0 323 006
A2

(12)

EUROPEAN PATENT APPLICATION

(21) Application number: 88309309.8

(51) Int. Cl.⁴: G02F 1/17

(22) Date of filing: 06.10.88

(33) Priority: 24.12.87 US 137631

(43) Date of publication of application:
05.07.89 Bulletin 89/27

(84) Designated Contracting States:
DE FR GB

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(54) New electrochromic device and method of making an electrochromic layer therefor.

EP 0 323 006 A2 (57) This invention teaches an electrochromic device in which an electrochromic layer is positioned between two electrodes. The electrochromic layer comprises an organic based bulk material which has been polymerized and condensed supporting electrochromic particles and ion producing particles in fixed but generally distributed positions therewithin. The bulk material permits migration of ions produced by the ion producing particles to and from the electrochromic particles upon change in voltage between the first and second electrodes. The bulk material also prohibits the passage of electrons therethrough when a voltage is applied between the first electrode and the second electrode, whereby an electric field

is built up between the first and second electrodes which causes migration of the ions. Also my invention is a method of making a material which can form an electrochromic layer. The method has the following steps. A gel producing organic material is dissolved in a solvent to produce a solution. The gel producing material is one which permits migration of ions therethrough but prohibits passage of electrons therethrough. A finely divided ion producing material is added to the solution. A finely divided electrochromic material is also added to the solution. The solution is thoroughly mixed. The solution is then polymerized and condensed to obtain a gelled material. The gelled material supports the finely divided

ion producing material and the finely divided electrochromic material in fixed but generally distributed position therewithin.

NEW ELECTROCHROMIC DEVICE AND METHOD OF MAKING AN ELECTROCHROMIC LAYER THEREFOR

This invention relates to a new electrochromic device and a method of making an electrochromic layer therefor.

Electrochromism is a coloring phenomenon observed in some materials when they are placed in the presence of an electrical field. Such materials are normally uncolored when no electrical field is present, but change to a colored state when an electrical field is placed therearound.

Such a material exhibiting reversible color changes is known as an electrochromic material (ECM). This electrical field dependent transition phenomenon from an uncolored state to a colored state is called optical switching. If a thin coating of such an ECM is placed on a glass support, the entire device is known as a switchable window. When no electrical field is placed on the ECM, it is uncolored and transparent and thus one can look through the window. On the other hand, when an electric field is placed on the ECM, it colors thereby reducing the amount of light transmitted through the window. The reduction of light transmission may be partial or total thereby either reducing the amount of light which passes through the window or eliminating it altogether.

Certain transition metal oxides are known to exhibit electrochromism. Materials such as tungsten oxide, molybdenum oxide, and vanadium oxide are known electrochromic materials.

Electrochromic materials can be divided into two categories depending on the mode of operation of the ECM. The ECM can be either a cathodic ECM or it can be an anodic ECM. The operation of these two types of ECM will be understood by reference to Figures 1 and 2.

In Figure 1, the operation of a cathodic ECM is schematically illustrated. In the cathodic case, an electrochromic material of the cathodic type is physically located next to a cathode which has been placed, for example, on a glass substrate. A fast ion conductor material, which produces light ions of a positive charge, for example, lithium ions, is placed between the electrochromic material and an anode which also may be placed on a glass substrate.

In the cathodic case, the electrochromic material is subjected to a reduction or gain of electrons when an electric field is applied thereto. Application of the electric field is indicated by the plurality of plus signs shown on the anode and the plurality of negative signs shown on the cathode. As a result of the application of an electric field applied between the anode and the cathode of appropriate strength and sign, positive light ions

are driven from the fast ion conductor into the electrochromic material and electrons are supplied to the electrochromic material from the cathode.

The positively charged light ions and the negatively charged electrons associate themselves with the electrochromic material to reduce the same thereby moving the electrochromic material from a base state to a reduced state. In the base state, the electrochromic material is uncolored, but in its reduced state, it is colored.

When the electric field is removed, the electrochromic material will return to its base state, that is, its uncolored state. The period of time required for return of the material to its uncolored state varies from material to material and is generally referred to as the memory of the ECM. Some materials have relatively short memories and others have prolonged memories.

While the operation of the cathodic material has been illustrated by the inclusion in the electrochromic material of positive light ions and negative electrons, the cathodic operation may also take place by the extraction of negative light ions and holes from the electrochromic material respectively to the fast ion conductor and the cathode.

Operation of an anodic ECM is schematically illustrated in Figure 2. In this case, the electrochromic material is located next to the anode and the fast ion conductor is located between the electrochromic material and the cathode. In the anodic operation, oxidation of the ECM takes place, that is, electrochromism occurs when the ECM loses electrons. The loss of electrons in this case is illustrated by the application of an electric field represented by a plurality of pluses on the anode and the plurality of minuses at the cathode.

In the case of an anodic ECM, when an electric field is applied between the anode and the cathode of appropriate strength and sign, negative light ions, such as hydroxyl ions, move from the fast ion conductor into the ECM, and holes move into the ECM from the anode. As a result of this movement, the ECM loses electrons thereby being oxidized away from its base or uncolored state to a colored state. Once again, the anodic material will return to its base state when the electric field is released. The time of return to its uncolored state again depends on the memory of the ECM.

The anodic ECM may also operate by extracting from the ECM positive light ions and negative electrons respectively to the fast ion conductor and the anode. In this case, the ECM is also oxidized to a colored state.

In general, in either the cathodic ECM or the anodic ECM, the coloring observed in the material

is an electrochemical phenomenon produced by the application of an electric field on the ECM to move it from a base condition to a nonbase condition. By applying a field of required strength and direction to cause activity in the ECM, polarization occurs within the entire electrochromic device. In such polarization, a disassociation of ions occurs in the fast ion conductor creating free light ions of the required charge. These light ions move into the ECM because of the electrical field. Once in the ECM, they bond themselves to the molecules of the ECM.

As has been described above, depending on the charge of the bonding ion and its associated electron or hole, oxidation or reduction of the ECM occurs. These ECM materials are normally multivalent state materials exhibiting different optical absorption and dispersion spectra corresponding to different oxidation states. For these ECM's, these different oxidation and reduction states are all stable under appropriate electric field conditions.

In the base ECM, the metal valence states are generally at the maximum, whereby such metal oxides in their base state exhibit the lowest optical absorption. They are generally good insulators with high energy gaps, optically transparent and colorless in such a condition. On the other hand, oxygen deficient oxides as well as the lower valance state oxides created as a result of the application of an electric field exhibit higher optical absorption than those of base oxides. When oxygen deficient, ECM's exhibit a selective absorption when they are in one of their lower valance state oxides. Different ECM exhibit different colors, depending upon the spectral location of the selective absorption bands of that particular oxygen deficient metal oxide.

The explanation so far set forth above of cathodic and anodic ECM is my best explanation. It is possible to reduce this theory of mine to electrochemical equations in which a base ECM, acting as a cathodic material, would be subjected to a reduction by inclusion in the ECM of positive light ions and negative electrons or by extraction from the ECM of negative light ions and holes respectively to the fast ion conductor and the cathode in order to reduce the cathodic ECM to its colored state.

In a similar manner, an electrochemical equation may be written for an anodic ECM in the same manner. In this case, the inclusion of negative light ions and holes in the ECM or the extraction of positive light ions and negative electrons respectively to the fast ion conductor and the anode is sufficient to oxidize the anodic material to a colored state.

U.S. patent 4,298,448 issued on Nov. 3, 1981 for an "Electrophoretic Display". This patent discloses an electrophoretic display including a cell

having two plates spaced apart and provided at least regionally with electrodes. At least one of the plates and an associated electrode facing an observer are transparent. The cell contains a suspension consisting of an inert dielectric liquid phase and a dispersed solid phase which at least in part are optically discriminate electrophoretic particles. The individual electrophoretic particles each are of practically the same density as the liquid phase. At least some of the electrophoretic particles are provided with a coating or organic material which is solid at the cell operating temperature but which melts at higher temperatures. The coating contains at least one charge control agent, preferably a salt of a divalent metal or metal of higher valency and of an organic acid, which imparts a well defined, uniform surface charge and a well defined, uniform surface potential to the particles. In essence, this patent teaches a very difficult to prepare electrophoretic display device.

U.S. patent 4,652,090 issued on March 24, 1987 for a "Dispersed Iridium Based Complementary Electrochromic Device". This patent discloses an electrochromic device including one electrode layer, a cathodically coloring electrochromic layer, an ion conductive layer if required, a reversibly oxidizable layer and another electrode layer. At least one of the electrode layers is transparent. At least one of the cathodically coloring electrochromic layer, the ionic conductive layer and the reversibly oxidizable layer is adapted to contain protons or include a proton source for emitting protons upon application of a voltage. The reversibly oxidizable layer comprises a transparent dispersion layer which is made by vacuum thin film formation techniques of thick-film processes and comprises a metal iridium, iridium oxide or iridium hydroxide disperse phase and a transparent solid dispersion medium. As an alternate, the reversibly oxidizable layer and the other electrode are replaced with a single transparent conductive dispersion material layer which is made by vacuum thin film formation techniques of thick-film formation techniques or thick-film processes and comprises a metal iridium, iridium oxide or iridium hydroxide disperse phase and a transparent solid dispersion medium.

According to the present invention, there is provided an electrochromic device comprising a first electrode, a second electrode and an electrochromic layer between said first and said second electrodes said layer comprising, an organic based bulk material which has been polymerized and condensed supporting electrochromic particles and ion producing particles in fixed but generally distributed positions therewithin, said bulk material permitting migration of ions produced by said ion producing particles to and from said electrochromic

particles upon change in voltage between said first and second electrode, said bulk material also prohibiting the passage of electrons therethrough when a voltage is applied between said first electrode and said second electrode, whereby an electric field is built up between said first and second electrodes which causes migration of said ions.

Further according to the present invention, there is provided a method making a material which can form an electrochromic layer which comprises the steps of dissolving a gel producing organic material in a solvent therefor to produce a solution, said gel producing organic material permitting migration of ions therethrough but prohibiting passage of electrons therethrough, adding a finely divided ion producing material to said solution, adding a finely divided electrochromic material to said solution, mixing said solution thoroughly, and polymerizing and condensing said solution to obtain a gelled material, said gelled material supporting said finely divided ion producing material and said finely divided electrochromic material in fixed but generally distributed positions therewithin.

It is an advantage of this invention that a new electrochromic device is provided in which both electrochromic particles and ion producing particles are supported in the same matrix.

In accordance with details of preferred embodiments of the invention, one or both of the electrodes are transparent electrodes. Preferably the organic based bulk material is polyvinylbutyral. The electrochromic particles may be anodic electrochromic particles or cathodic electrochromic particles or even mixtures of the two types of electrochromic particles. Preferably, all of the anodic or cathodic electrochromic particles are the same.

The invention will now be described further, the way of example, with reference to the accompanying drawings, in which:

Figures 1 and 2, as previously discussed, are schematic illustrations respectively of the operation of a cathodic electrochromic device and of an anodic electrochromic device.

Figure 3 is a schematic illustration of an operational mode of an electrochromic device embodying this invention.

Figure 4 and 5 are enlarged schematic illustrations of a matrix material used in the electrochromic device of Figure 3 showing in Figure 4 the matrix material without an electric field applied thereto and in Figure 5 the matrix material with an electric field applied thereto.

Figures 3 through 5 schematically illustrate the electrochromic device of this invention. Figure 4 illustrates the matrix material with no electric field present and Figure 5 illustrates the matrix material with an electric field present. The electrochromic

device may be fabricated to have anodic electrochromic properties of cathodic electrochromic properties, or both, as desired.

Reference is now made to Figure 3. In this preferred embodiment, an anodic ECM is disclosed. A first glass sheet has an anode thereon and a second glass sheet has a cathode thereon. In both cases, in accordance with the preferred embodiment of this invention, the glass sheets have a thickness of .3cm (1/8th inch) and the electrodes have a thickness of about 200 angstroms. In accordance with the teachings of the preferred embodiment, both the anode and the cathode are formed from tin oxide doped with fluorine. Such a coating may be applied to the glass sheet by a pyrolytic process, as is well-known in the art. It is, of course, apparent that other electrode materials may be used and other materials may be substituted for the glass sheets, for example, quartz, plastic, etc. Generally, one, or both, of the electrode supports should be transparent so that the colors developed in the electrochromic material may be viewed.

As shown in Figure 3 in the preferred embodiment, a matrix material is provided that supports therein both finely divided ion producing material and finely divided electrochromic material between the cathode and the anode. Three examples of the preparation of the matrix material supporting therein both finely divided ion producing material and finely divided electrochromic material will be set forth below.

35 Example 1

The matrix material was prepared by dissolving fifteen percent (15%) by weight polyvinylbutyral powder (B-90) with eighty five percent (85%) by weight of a methanol acetone mixture to form a solution. Normally the powder forms from ten percent (10%) to twenty percent (20%) by weight of the solution. The polyvinylbutyral powder was purchased from Monsanto Company as B-90 powder. The gelled polyvinylbutyral is an ionic conductor but not an electronic conductor. The acetone methanol mixture was five percent (5%) by volume acetone.

A finely divided ion producing material was added to the solution. The preferred ion producing material was lithium chloride (LiCl). This material was added to the solution in an amount of 0.5% by weight of the solution. The ion producing material may be added up to the point that it saturates the solution. Other ion producing material include NaCl, KCl, LiBr, LiI, NaBr, KBr, LiF, NaF, KF, cryolite, as well as strong bases such as NaOH and KOH. Placement of the ion producing materials in the

solution improves the ionic conduction of the material produced by the solution.

A finely divided electrochromic material is also added to the solution. In this Example the material added is electrochromic lead oxide. The amount of lead oxide added to the solution is the amount of lead oxide it would be required to produce a layer having a thickness of 4000 Å on one of the electrodes. A range of lead oxide additions would be sufficient lead oxide to produce a layer having a thickness in a range from 3000 Å to 5000 Å. The electrochromic lead oxide is a cathodic electrochromic material.

The solution so formed is then thoroughly mixed. The solution polymerizes and condenses while being stirred at room temperature to produce a gelled matrix material supporting therein the finely divided ion producing material and the finely divided electrochromic material in fixed but generally distributed positions.

The gelled matrix material supporting therein the finely divided ion producing material and the finely divided electrochromic material in fixed but generally distributed positions is then positioned between the two electrodes as is shown in Figure 3. The matrix material has a thickness which depends on the type of material used and the type of materials added thereto. In the preferred case, the matrix has a thickness of about 0.1mm. Since electrochromic lead oxide is a cathodic material, when a negative five volts was applied between the anode and the cathode, a grey color resulted in the electrochromic device.

The production of the grey color may be explained by aid of Figures 4 and 5. Figure 4 shows a schematic illustration of the matrix containing the finely divided ion producing material (LI) and the finely divided electrochromic material in a condition where no voltage is applied to the anode and the cathode of the electrochromic device of Figure 3. In this case the electrochromic particles do not have a charge associated therewith and the ions, both positive and negative, are randomly positioned.

When the voltage is applied to the electrochromic device as described above, then the electrochromic particles do have a charge associated therewith as shown in Figure 5 by the plus and minus signs on the polarized electrochromic particles. When this charging occurs, positive light ions are drawn to the negative end of the electrochromic particles and negative light ions are drawn to the positive end of the electrochromic particles. This action causes a reduction of the negatively charged side of the electrochromic lead oxide and results in the production of the grey color.

Example 2

The procedure of Example 1 is followed except that the solvent used to form the solution was five percent (5%) by volume isopropanol and ninety five percent (95%) by volume methanol. The electrochromic material used was electrochromic bismuth oxide. Electrochromic bismuth oxide is a cathodic electrochromic material. Thus when it is formed into an electrochromic device such as shown in Figure 3, it will take on a grey color when a negative two volts is applied between the anode and the cathode of the device.

Example 3

The procedure of Example 1 is followed except that the solvent used to form the solution was dipropylene glycol methyl ether (DPM). The electrochromic material used was electrochromic iridium oxide. Electrochromic iridium oxide is an anodic electrochromic material. Thus when it is formed into an electrochromic device such as shown in Figure 3, it will take on a blue black color when a positive two volts is applied between the anode and the cathode of the device.

While the Examples above show the use of either anodic or cathodic electrochromic particles embedded in the matrix, it is possible to embed both types of particles in the matrix at the same time. If this is done, it is preferred that the two types of particles have about the same switching times between their uncolored and colored states. Also, if just anodic or cathodic particles are to be used, the particles may be mixtures of various types of anodic or cathodic materials. Again it is preferred that the various types of particles have about the same switching times between their uncolored and colored states.

While polyvinylbutyral was used in the Examples as the major material for forming the gelled matrix material, other similar materials may be used. For example materials such as polyvinylacetate, polymethacrylates, urethanes, acrylics, etc. which may be used.

Claims

- An electrochromic device comprising a first electrode, a second electrode and an electrochromic layer between said first and said second electrodes said layer comprising, an organic based bulk material which has been polymerized and condensed supporting electrochromic particles and ion producing particles in fixed but generally distributed positions therewithin, said bulk material

permitting migration of ions produced by said ion producing particles to and from said electrochromic particles upon change in voltage between said first and second electrode, said bulk material also prohibiting the passage of electrons therethrough when a voltage is applied between said first electrode and said second electrode, whereby an electric field is built up between said first and second electrodes which causes migration of said ions.

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2. A device as claimed in Claim 1, wherein at least one of said first or second electrodes is a transparent electrode.

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3. A device as claimed in Claim 1 or 2, wherein said organic based bulk material is gelled polyvinylbutyral.

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4. A device as claimed in any one of Claims 1 to 3, wherein said electrochromic particles are cathodic electrochromic particles, anodic electrochromic particles or a mixture of both anodic cathodic electrochromic particles.

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5. A device as claimed in Claim 4, wherein said anodic electrochromic particles are all the same and/or said cathodic electrochromic particles are all the same.

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6. A method making a material which can form an electrochromic layer which comprises the steps of dissolving a gel producing organic material in a solvent therefor to produce a solution, said gel producing organic material permitting migration of ions therethrough but prohibiting passage of electrons therethrough, adding a finely divided ion producing material to said solution, adding a finely divided electrochromic material to said solution, mixing said solution thoroughly, and polymerizing and condensing said solution to obtain a gelled material, said gelled material supporting said finely divided ion producing material and said finely divided electrochromic material in fixed but generally distributed positions therewithin.

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7. A method as claimed in Claim 6, wherein said finely divided electrochromic material is an anodic electrochromic material or a mixture of both anodic electrochromic material and cathodic electrochromic material.

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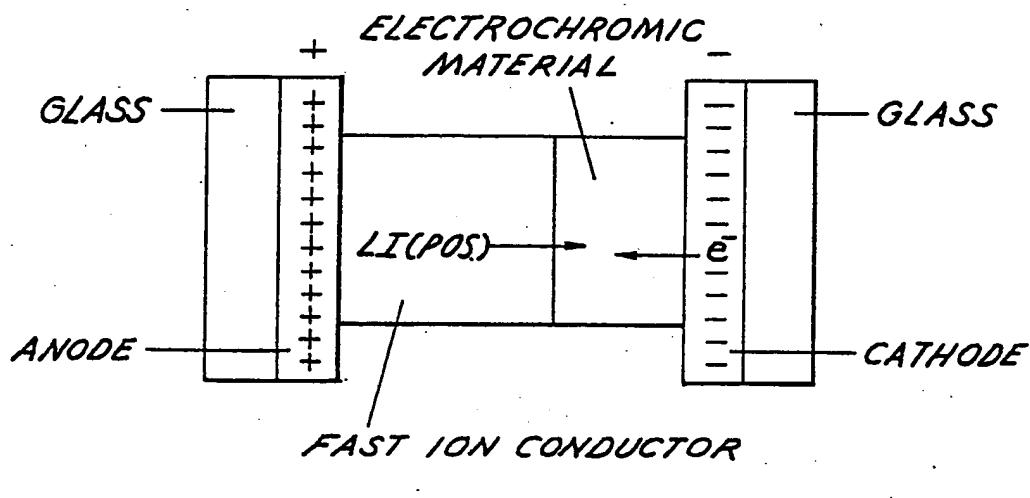
8. A method as claimed in Claim 7, wherein said finely divided anodic electrochromic material is all the same and/or said finely divided cathodic electrochromic material is all the same.

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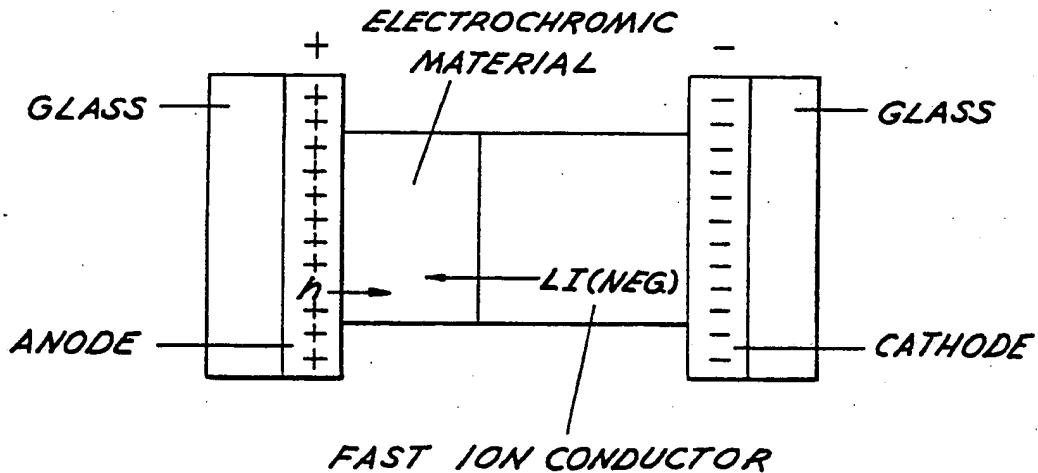
9. A method as claimed in any one of Claims 6 to 8, wherein said organic based bulk material is gelled polyvinylbutyral.

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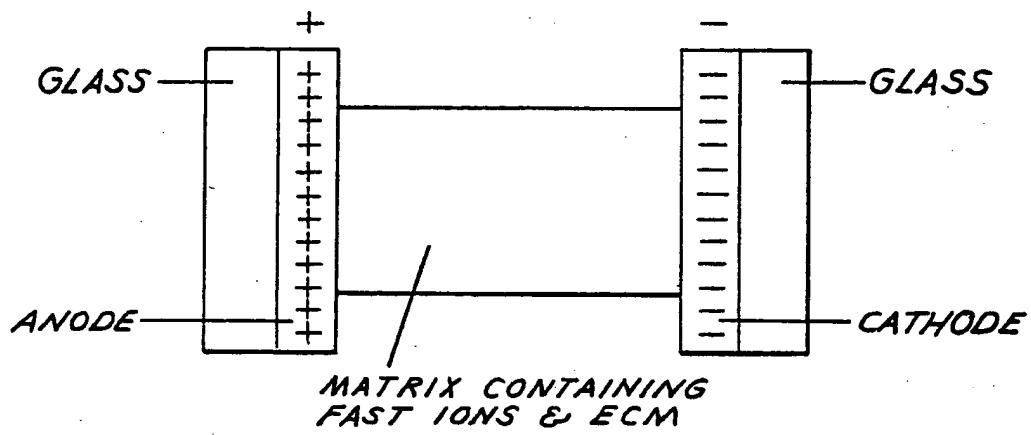
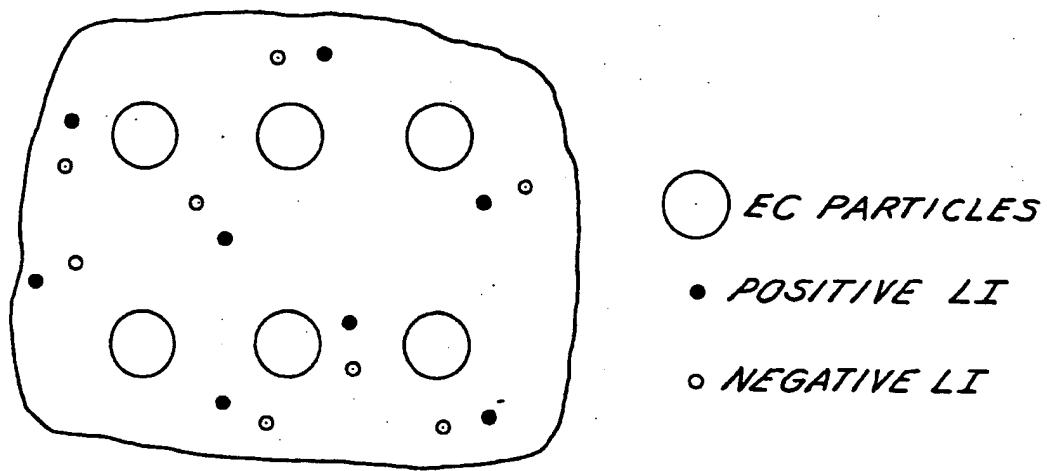
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FIG.1 CATHODIC MATERIAL

**REDUCTION - GAIN OF ELECTRONS
OR $Li^{(NEG.)}$ AND e^- (NEG.) INCLUSION
 $Li^{(POS.)}$ AND HOLE EXTRACTION**

FIG.2 ANODIC MATERIAL

**OXIDATION - LOSS OF ELECTRONS
OR $Li^{(POS.)}$ AND HOLE INCLUSION
 $Li^{(NEG.)}$ AND e^- (NEG.) EXTRACTION**

FIG.3FIG.4FIG.5